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Changes in the Electronic Structure Related to the Ni2MnGa Martensitic Phase Transformation

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Abstract:

Synchrotron-radiation-based photoelectron spectroscopy has been used to probe the electronic structure of Ni_2MnGa. In particular, the variation of the valence band at temperatures near the transformation temperature for the martensite has been followed. Two salient results have been obtained. (1) The valence electronic structure does not seem to vary in the temperature region associated with phonon softening (near room temperature). (2) Changes in the electronic structure at the lower (martensitic) transformation temperature (T_M=220K) have been observed, which agree with theoretical density of states calculation. These changes are indicative of Fermi Surface Nesting.

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Martensitic phase transformations have been extensively studied for over a century because of the importance of the product phase in metallurgy and the key role played by martensitic transformations in the shape memory phenomenon. Many metallic alloys are known to undergo a martensitic phase transition: a displacive, diffusionless first-order transformation from the symmetric high-temperature parent phase to a low-symmetry martensite structure upon cooling [1]. These phase transitions are often associated with phonon anomalies in the parent phase: particularly, in bcc-like materials the $[\zeta\zeta 0]$ TA_2 mode with displacement along $[1\bar{1}0]$ softens at a certain wave vector ζ_0, which is close to reciprocal-lattice vector of the low-temperature structure. This has been demonstrated in extensive studies of Ni-Ti [2-5], Ni-Al [6-9], and Au-Cd [10]. Experimental results were found to be in excellent agreement with theoretical calculations, which attributed the phonon softening to electron-phonon coupling and specific nesting properties of the Fermi surface [11,12]. One interesting candidate to study is the Ni_2MnGa intermetallic shape-memory alloy, which, among the large variety of ferromagnetic Heusler alloys, is the only one known to undergo a martensitic phase transition. Thermally and stress-induced martensitic structures have been investigated in this system by x-ray diffraction [13,14], electron diffraction and microscopy [11,15], ultrasound experiments [15,16,17], magnetoelastic measurements [16,18], and inelastic neutron scattering and neutron diffraction [19,20]. A significant and nearly complete softening of the transverse acoustic phonon mode, suggested by Fritsch *et al.* [21], has been observed in the parent phase. In addition a new premartensitic phase transition was observed. However, its relation to the low-temperature martensitic transition is not fully understood. At room temperature Ni_2MnGa has an fcc $L2_1$ Heusler structure. The phonon softening occurs between 400 K (~130°C) and 260 K. (~-10°C), while the martenistic phase transition temperature is ~220 K (~ -50°C). The alloy also shows a magnetic ordering transition with a Curie temperature of 376 K (~100°C) [22].

Angle-resolved photoelectron spectroscopy (ARPES) has proven to be a very powerful method to investigate changes in the electronic structure of materials. For example, it has revealed changes in the surface electronic states of hydrogen on W(110) [23], and changes in the spin-orbit splitting of valence states induced at surfaces by adsorbates [24], which are also related to phonon softening and Fermi surface nesting. ARPES has also been used to measure the exchange splitting between the upper and lower *d*-band in Ni, [25] and changes in the electronic structures of thin alloy films on Cu [26].

Returning to issue of Ni_2MnGa, the analytical potential of ARPES begs an important question: “Will there be electronic structure variations associated with the phonon softening or will they be concomitant with the phase transformation?” Another way to put this would be: “ Do electronic structure changes, associated with the martenistic phase transformation, follow or lead the phonon softening?” To address these questions, synchrotron- radiation-based photoelectron spectroscopy has been performed upon Ni_2MnGa.

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The experiments were carried out at Beam-Line 7.0.1 [27] at the Advanced Light Source in Berkeley, CA, USA. Measurements were performed in both the “XPD” [28] and “SPIN” [29, 30] Spectrometers on Beam-Line 7.0. Sample temperatures could be varied over a wide range. The cooling is achieved via liquid nitrogen refrigeration. The heating is done using an electron-beam heating apparatus behind the sample. The studies of electronic structure were carried out at high resolution, in order to observe the energy-, angle-, and momentum-specific details of the Ni_2MnGa valence band structure. Typical energy and angular bandwidths were on the order of 0.1 eV and 2°, respectively. The bulk samples were prepared at LLNL, from high purity single crystals, with <100> normal. Surface crystallinity and composition were tested in situ using Low Energy Electron Diffraction (LEED) and X-ray Photoelectron Spectroscopy (XPS) with a $MgK\alpha$ Source. The LEED exhibited strong four-fold symmetric patterns at several kinetic energies, indicative of good ordering. The XPS scan showed the correct photoemission and Auger lines for Ni, Mn and Ga, with no evidence of oxygen or carbon contamination. However, it should be noted that the O1s and C1s cross sections [31] are fairly small at $h\nu$ = 1254 eV, giving rise to a limited sensitivity to oxygen and carbon contamination in this measurement. The relative intensities of the various Ni, Mn and Ga lines seem consistent with the bulk stoichiometry of 2:1:1.

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Angle-resolved photoemission is a nearly ideal tool with which to investigate the band structure of a material. By varying the azimuthal and polar angle as well as the excitation energy, one is able to study the dispersion of electronic states throughout the Brillouin zone. In this experiment, we aligned the sample in a way to be sensitive along the [□□0] direction when we varied the azimuthal angle. In our spectrometers, the angle between the incoming photons and outgoing (collected) electrons was fixed. The Pointing vector of the X-rays, the linear polarization of the X-rays, and the collection direction of the electrons were all in the same plane, referred to the experimental "horizontal" plane. The position of our ARPES measurements is shown in Figure 1. Here we have followed the Fermi Surface mapping of Zhao and Harmon [12] for $Ni_{0.625}Al_{0.375}$, to illustrate the k-space positions in our Ni_2MnGa experiments. For the ejected photoelectrons, the energy and momentum are related as follows. Of course, the vectorial components of the momentum depend upon the angles of emission relative to the crystalline axes.

$$KE_{IN} = h\nu - BE - \Phi + V_0 \qquad (1)$$

$$k_{IN} = 0.5124 \quad KE_{IN} \qquad (2)$$

Here, KE_{IN} is the kinetic energy of the electron inside the crystal, $h\nu$ is the photon energy, BE is the binding energy with respect to the Fermi Level, Φ is the work function, and V_0 is the inner potential.

The potential for Fermi Surface nesting is multiple in a system such as Ni_2MnGa. A martenistic phase transformation is a change of the lattice structure and therefore a concomitant variation of the Brillouin Zone, which itself could already lead to Fermi surface perturbations such as nesting. Furthermore, when the wave vector of the phonon disturbance has a magnitude of $2k_F$, this singularity should be conveyed via the screening ion-ion interaction into the phonon spectrum itself. This situation, in turn, could result in weak “kinks” at values corresponding to the external diameter of the Fermi surface [32]: in this case, the possibility of Fermi surface nesting. An example of a potential Fermi Surface Nesting is illustrated in Figure 1. Thus, an excellent starting point for the investigation of the variations in the valence electronic structure will be the parts of the Fermi Surface which might be likely to exhibit Fermi Nesting effects.

In the first series of measurements to be discussed, we investigated the dispersion of the electronic states along the [□□0] direction above and below the martensitic phase transformation (t □ -50°C): at room temperature (Fig. 2a) and at t □ -90°C (Fig. 2b). Here the photon energy was 165 eV. The angles shown along with the spectra in Figure 2 correspond to the green scale shown in Figure 1. At an angle of zero degrees, the emission is from near a □ point. Increasing the angle moves the k space position away from □ and towards a zone boundary. Measurements were also taken on the other side of the □ point, at angles with negative values. Although not shown, measurements at negative angles mirrored those at positive angles, symmetrically around □. For both temperatures we observed four main peaks in the spectra: A, B, C, and D as shown in Figure 2. Peaks B, C and D show a very similar dispersion for both high and low temperatures. Peak A is dispersing strongly at room temperature, while for the temperature below the martensitic phase transformation, there is hardly any dispersion visible. In fact, it may be that the weak A peak seen at t ≈ -90°C is merely the remnant Fermi edge. To test the dispersion dependence in the orthogonal direction, the emission angles were fixed to be near the zone boundary and the photon energy was varied, both at temperatures near room temperature and at t ≈ -90°C. (This data is not shown.) Again, similar energy relations were found for A: a strong, dispersive peak was observed at room temperature but at t ≈ -90°C, Peak A has essentially disappeared relative to the other features. Previous theoretical treatments of Ni_2MnGa can provide insight into what is happening here. Recent calculations by MacLaren [33] suggest significant but limited changes in the density of states when going through the martensitic phase transformation, e.g. changing from a cubic to a slightly distorted phase. They predict that the majority densities of states for both cubic and distorted are essentially identical. The majority bands are almost full, with the Fermi energy at zero. Hence it is not surprising that the changes in the density of states as a result of distorting the lattice are primarily confined to the minority spin channel. In this case, the Fermi energy passes through a region that is predominantly occupied Ni d-states and unoccupied Mn d-states. The picture of the bonding in Ni_2MnGa suggested by MacLaren is also quite similar to that described for Ni_2MnGa by Godlevsky and Rabe [34]. Their calculations show that as the crystal is distorted, the minority density of states is perturbed:

The peak just below the Fermi energy broadens, transferring spectral weight out of occupied Ni d-states, that in turn leads to an overall slight decrease in the cohesive energy of the crystal. In our spectra, peak A represents the peak just below the Fermi energy (probably the Ni minority peak), where we can observe the transfer of spectral weight when going from the cubic to the distorted phase. The other peaks are the occupied Ni and Mn peaks. Although angle-resolved photoemission does not represent fully the density of states, but only a partial density of states, we can observe the same trend as predicted previously by theoretical calculations.

In another set of measurements, the temperature dependence was probed more directly. A series of photoelectron spectra were collected. In this series, the sample was first cooled (Fig. 3a) and then heated (Fig. 3b). It is immediately obvious that there is a significant temperature dependence to the collected spectra, particularly at the Fermi Energy. While peaks B,C and D appear to be fairly unperturbed by the temperature variations, peak A is strongly affected. In addition, we observe a temperature hysteresis. The variations do correspond to the martenistic phase transformation temperatures T_M = 212 K (t ≈ -60°C) on cooling and 228 K (t ≈ -45°C) on warming up, as measured with neutron scattering experiments [20]. In this temperature dependent study, we have no indications for changes in the electronic structure associated with the phonon anomaly, but only for changes in the electronic structure related to the martenistic phase transformation. This softening of the phonon branch along the

[□□0] direction occurs in the temperature range 400K (t ≈ 130°C) to 230 K (t ≈ -40°C). There is a possible explanation for the lack of change in our spectra. Changes in the electronic structure due to phonon softening are very small [23,24], and the onset of the phonon softening occurs in Ni_2MnGa at 400 K (t ≈ 130°C). It is also possible that at these temperatures the energy resolution was not sufficient to resolve the small changes associated with the phonon softening or that we are looking in the wrong part of the Brillioun Zone.

In summary, we observe changes in the electronic structure related to the martensitic phase transformation (i.e., the changes in crystal structure), which shows the predicted temperature hysteresis. We also are able to observe the transfer of spectral weight in our photoemission spectra, which agree with calculated density of states of Ni2MnGa. To clearly understand the role of the phonon softening related to the electronic structure, it is necessary to study the complete Fermi surface energy and angle dependence with a very good energy and angular resolution, over a broader range of momentum and energy space.

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<u>Figure Captions</u>

1. The positions in k-space are shown here, along with some possible nesting sites. These projections of the Brillouin Zone are for Ni_2MnGa, following the □-phase of of $Ni_{5/8}Al_{3/8}$ alloy in Reference 12. A map in green has been superimposed, showing the positions and coordinates of our photoemission measurements in momentum space, for the Ni_2MnGa system, as a function of angle. The red square defines the Brillioun Zone, in which the photoemission measurements are made. To illustrate the potential for nesting, the Fermi surfaces $Ni_{5/8}Al_{3/8}$ alloy (from Reference 12) in the k_x – k_y plane with different values of k_z (0.25 □/a, 0.38 □/a, 0.48 □/a) are shown. The arrow indicates two nested surfaces.
2. Shown here are two sets of photoelectron spectra, one taken at room temperature (topmost, Figure 2a) and another at low temperature (lower, Figure 2b, t = -90°C). The photon energy was 165 eV. The positions in k space correspond to those shown in Figure 1. The vertical axes are intensity in arbitrary units and the horizontal axis is BE (eV), or binding energy with respect to the Fermi Level. Within each set, the azimuthal angle (□) is varied, producing scans versus angle. From this it is possible to see the dispersion (variation of peak binding energy) and/or intensity oscillations with angle.

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3. Shown here are two series of high resolution photoelectron spectroscopy scans, taken with $h\nu$ = 165 eV. The position in k space corresponds to the zone boundary in Figure 1, where the potential nesting is shown with an arrow. The sample was alternately cooled and warmed, through the critical temperature regime. The topmost panel (Figure 3a) shows the result of cooling, while the lower panel (Figure 3b) shows the result of warming. The marked changes, especially at the Fermi Level, occur near T_M = 220K (t~-50°C).

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Figure 1

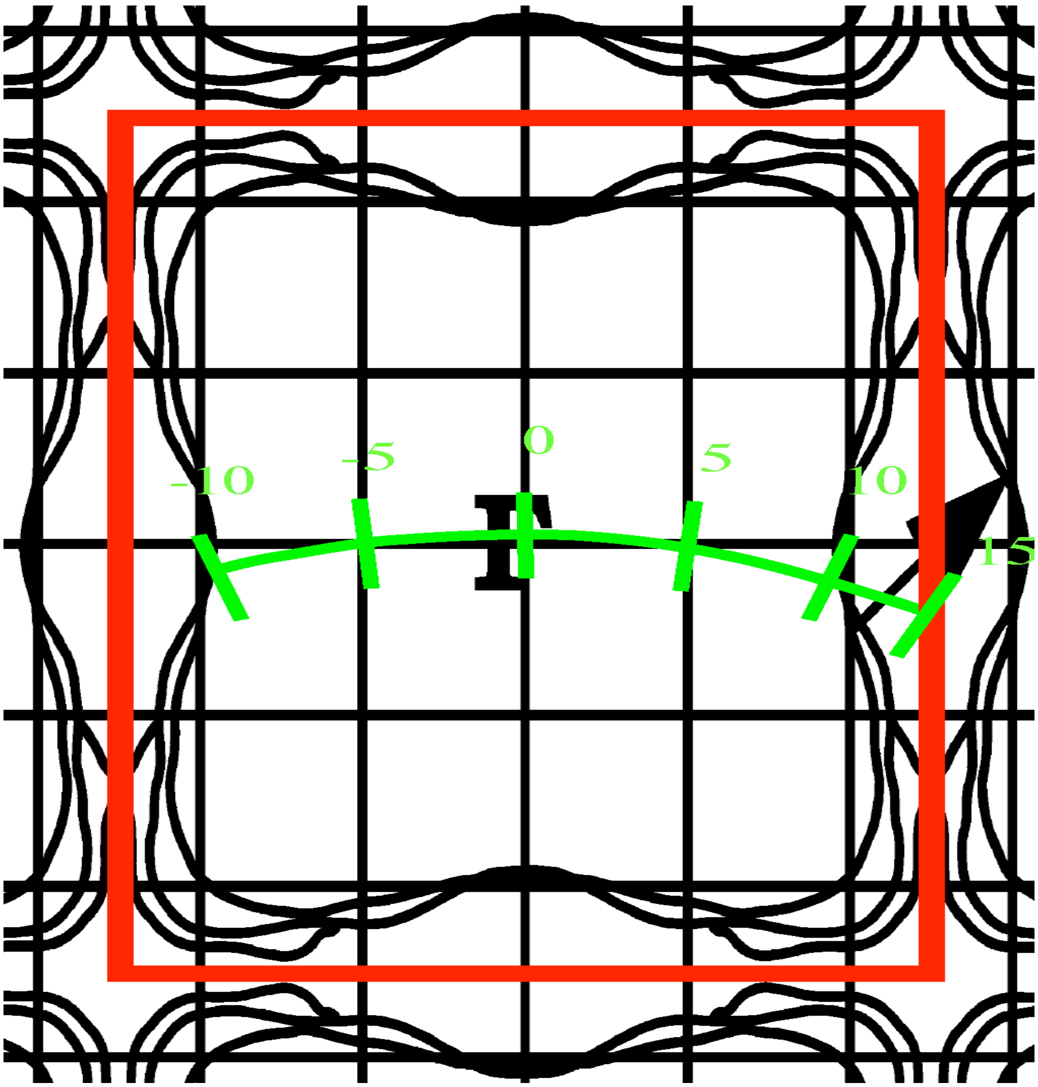

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Figure 2

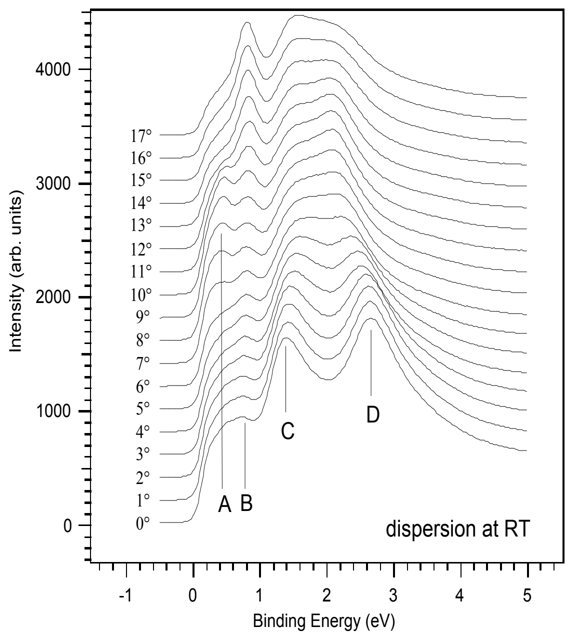

Figure 2a

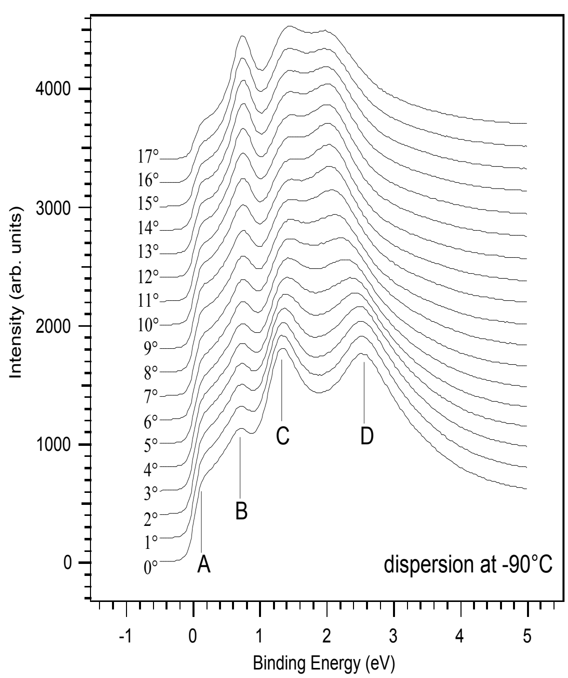

Figure 2b

Figure 3

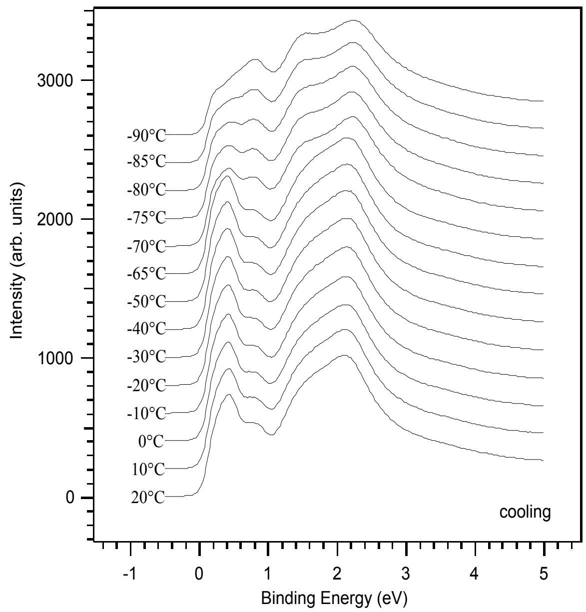

Figure 3a

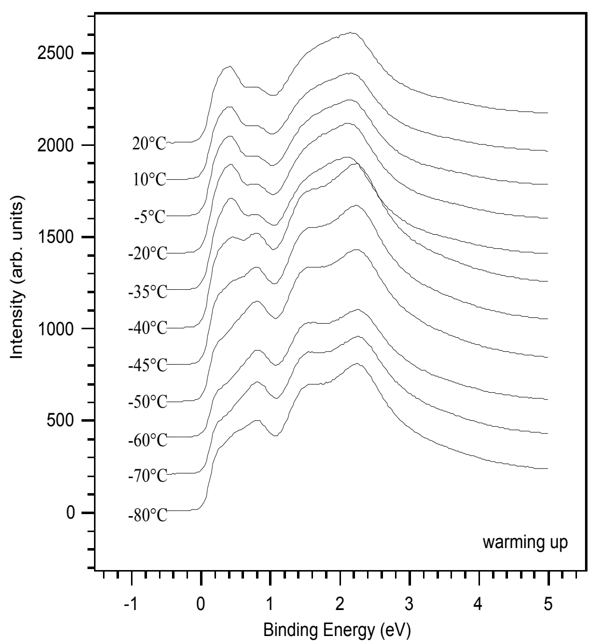

Figure 3b